Nutrient Status and Toxicity Problems in Acid Soils

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1 Introduction

For the purposes of this chapter, an acid soil will be considered as one with a pH value below 7, although serious problems associated with soil acidity are seldom encountered above a pH value of 5.5. Such soils can be very broadly grouped into those the acidity of which stems largely from natural weathering processes and those in which acidity has developed anthropogenically. The major difference between these two groups lies in the mineralogical composition of the clay fraction with the former typically being dominated by kaolinitic, sesquioxidic mineralogy and the latter by a less weathered suite of minerals including a significant 2:1 layer silicate component. This difference in mineralogical composition becomes important in the management of acid soils because the variable charge developed in the former group changes markedly with pH thus having a far greater influence on the capacity of the soil to hold nutrients than in the latter.

Before proceeding to explore the processes which take place as soils become more acid, it is necessary to carefully define and distinguish between a number of terms frequently used in describing nutrients in soils. Many soils contain sufficient total quantities of most essential elements to sustain adequate growth of crops but nutritional problems arise as a result of desorption/solubility/availability considerations. *Availability*, which has been very misused and seldom defined, must refer to those categories of nutrients in soils which a particular root system is able to extract in a given time. There is little ambiguity in such a definition but the problem in the use of this term arises when we attempt to measure these categories in the laboratory or greenhouse. Chemically assayed nutrients termed "available" need not and seldom are uniquely related to the amounts extracted by roots. There can be little question that what is present in the soil solution is available to the crop instantaneously but the manner in which the solution is replenished is not readily and unambiguously measured. Most techniques of testing soils for so-called available nutrients rely on extractants which remove the more readily soluble fractions present. Rather than terming these fractions available, one should label them extractable using a particular

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technique and reserve the term *available* for situations where actual roots are used in field situations to demonstrate response through plant performance.

Because changes in soil reaction can bring about marked changes in the desorption/solubility of many essential elements, a distinction between desorption/solubility and availability should be made. Desorption/solubility (unqualified) should be reserved for situations where the soil solution (or perhaps water extracts) are being studied. This approach is gaining favour of late particularly in attempting to describe the nature and consequences of soil acidity and will be used in the discussions to follow. Thus a nutrient may be soluble in the soil solution at levels adequate for plant nutrition but may be unavailable because the effects of other elements may prevent it from being assimilated by roots. The kinetics of the replenishment of the soil solution are extremely important in determining the quantity of a nutrient which can be supplied to the root system. Provided the replenishment kinetics are sufficiently fast, the composition of the soil solution should reflect the nutrient status of a soil fairly well. However, some soils may not be able to resupply the soil solution to meet the plant's requirements fast enough or may even be virtually deficient in a particular nutrient. Thus one needs some knowledge of the soil's supplying power or buffer capacity in order to interpret the levels of nutrients in the soil solution.

However, the effects of acidity on essential nutrients in soils are most suitably reflected by the soil solution as it is in this medium that all the reactions take place. Unless the nutrients pass through the solution phase, it is unlikely that they can be taken up by roots. The levels of many of the essential and toxic elements in soils are determined by desorption from or the solubilities of one or other solid phases and changes in acidity cause marked shifts in the equilibria. For others, the soil solution concentrations are governed by organic transformations, which are less appropriately reflected in the composition of equilibrium soil solutions because of the ephemeral nature of these reactions.

Most previous treatises on soil acidity have dealt with the subject mainly from the perspective of the solid phase with little attention being paid to the importance of the composition of the soil solution. To address this imbalance, the present discussion will be confined mainly to the soil solution in dynamic equilibrium with the solid phase with the objective of painting a somewhat different picture of the subject.

2 Soil Acidity and Nutrient Status

Soil acidity is of paramount importance in determining the amount of nutrient in solution and thus availability of essential elements in soils. To illustrate this point, examples of the types of reactions of elements important in plant nutrition with H^+ ions (Table 1) and the way in which the activities of various ions in the soil solution change as a function of pH (Fig. 1), are presented for soil systems dominated by inorganic colloid surfaces. For a number of nutrients the presence

Table 1. Effect of acidity on some soil reactions of elements important in plant nutrition (compiled from Lindsay 1972, 1979)

Element	Reaction with H^+
N	$R\text{-}NH_2 + 2O_2 \rightarrow R\text{-}OH + H^+ + NO_3^-$
	$2HNO_3 + 10H^+ \rightarrow N_2 + 6H_2O$
P	$Soil\text{-}Fe(OH)_3(s) + H^+ + H_2PO_4^- \rightleftarrows Soil\ FePO_4 \cdot 2H_2O(s) + H_2O$
	$Ca_5(PO_4)_3OH(s) + 7H^+ \rightleftarrows 5Ca^{2+} + 3H_2PO_4^- + H_2O$
K	$KAl_2(AlSi_3O_{10})(OH)_2 + 10H^+ \rightleftarrows K^+ + 3Al^{3+} + 3H_4SiO_4^0$
Ca	$CaCO_3(s) + 2H^+ \rightleftarrows Ca^{2+} + H_2O + CO_2$
Mg	$MgCO_3(s) + 2H^+ \rightleftarrows Mg^{2+} + H_2O + CO_2$
	$Mg_3Si_4O_{10}(OH)_2 \cdot 2H_2O + 6H^+ \rightleftarrows 3Mg^{2+} + 4H_4SiO_4^0$
S	$KAl_3(SO_4)_2(OH)_6(s) + 6H^+ \rightleftarrows K^+ + 3Al^{3+} + 2SO_4^{2-} + 6H_2O$
	$R\text{-}SH_2 + 2O_2 \rightarrow R + 2H^+ + SO_4^{2-}$
Cu	$Soil\text{-}Cu(s) + 2H^+ \rightleftarrows Cu^{2+} + Soil\text{-}2H(s)$
Zn	$Soil\text{-}Zn(s) + 2H^+ \rightleftarrows Zn^{2+} + Soil\text{-}2H(s)$
Mn	$MnO_2(s) + 4H^+ + 2e^- \rightleftarrows Mn^{2+} + 2H_2O$
Fe	$Soil\text{-}Fe(OH)_3(s) + 3H^+ \rightleftarrows Fe^{3+} + 3H_2O$
	$Soil\text{-}Fe(OH)_3(s) + 3H^+ + e^- \rightleftarrows Fe^{2+} + 3H_2O$
B	$Soil(Al,Fe)O\text{-}H_2BO_3(s) + H_2O + H^+ \rightleftarrows Soil(Al,Fe)O\text{-}OH_2^+ + H_3BO_3$
Mo	$2Fe(OH)_3(s) + 3MoO_4^{2-} + 6H^+ \rightleftarrows Fe_2(MoO_4)_3(s) + 6H_2O$
Si	$Al_2Si_2O_5(OH)_4(s) + 6H^+ \rightleftarrows 2Al^{3+} + 2H_4SiO_4^0 + H_2O$
Al	$Al(OH)_3(s) + 3H^+ \rightleftarrows Al^{3+} + 3H_2O$
CEC/AEC	$Soil\text{-}O^- + H^+ \rightleftarrows Soil\text{-}OH^0 + H^+ \rightleftarrows Soil\text{-}OH_2^+$
Exchange	$Soil\text{-}M^{n+} + nH^+ \rightleftarrows Soil\text{-}H_n^+ + M^{n+}$

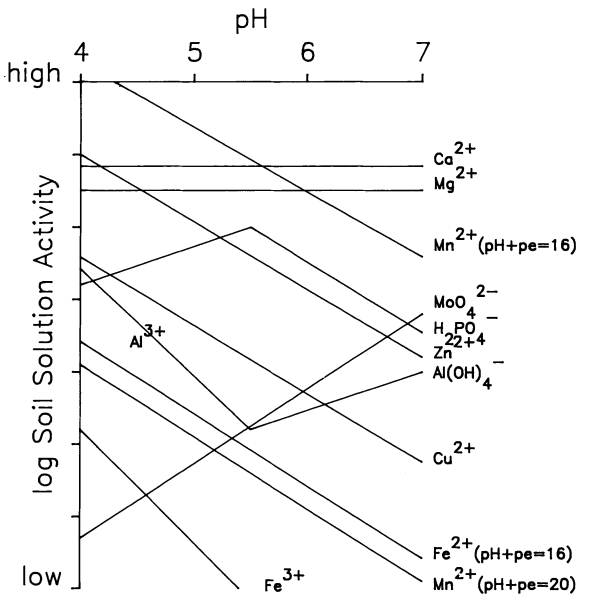

Fig. 1. Effect of pH on solution activity of some elements important in plant nutrition (After Lindsay 1972, 1979)

of organic matter may drastically change the relationship. Thermodynamic stability considerations have been used in the construction of Fig. 1 to illustrate the way in which nutrient levels in the soil solution change with pH. No attempt is being made to suggest that these equilibria are governed by simple solubility principles. In many cases sorption has been shown to be the likely mechanism involved. In addition, many different kinds of surfaces are in equilibrium with nutrients in solution and the selection of a particular solid surface implied in Fig. 1 does not mean that it is controlling alone. Nevertheless the level of nutrient in solution will vary in the same direction with changing pH irrespective of the mechanism or surface involved. This diagram has been presented as a qualitative model to better represent the effect of pH on nutrients in the soil solution and hopefully as a replacement for the simplistic diagram faithfully reproduced in books for the past 50 years (Pettinger 1935). To facilitate the discussion of the effects of acidity on nutrient status, each element will be discussed separately.

2.1 Nitrogen

Acidity, by virtue of governing the kinds, numbers and activities of microorganisms, regulates the rate of organic matter mineralization and therefore reduces the number of simple organic molecules available for further decomposition to render N and other constituent elements (P, S, etc.) soluble (Alexander 1980). Thus under very acid conditions, organic matter accumulates giving rise to vast storehouses of nutrients which can be exploited by liming.

The first reaction in Table 1 represents the transformation of organic N through all the intermediate steps to the formation of nitrate. Overall this reaction generates acidity which ultimately will lead to the cessation of nitrification due to the inability of the nitrifying organisms to perform their role under such conditions. Nitrification is markedly reduced below pH 6 and is undetectable below pH 4.5 (Alexander 1980; Adams and Martin 1984). On the other hand, ammonification reactions are insensitive to acidity over the range of pH found in most agricultural soils. Thus the effect of acidity on the soluble N status of most agricultural soils is limited to nitrification which means that for crops which are indifferent to N source (can use NH_4-N or NO_3-N) acidity plays little role in determining N availability. For sensitive crops (unable to use NH_4-N), acidification can result in restricted N uptake or even NH_4^+ toxicity.

The second reaction, illustrating denitrification, has been shown to be important in most agricultural soils (Bremner 1978). This reaction which consumes acidity results in the gaseous loss of N but probably assists in dissipating part of the acidity generated during nitrification under natural conditions.

In addition to direct effects on N transformations in soils, acidity has a deleterious effect on the symbiotic relationship between rhizobia and legumes. Generally, in soils with pH values below 6, poor nodulation and N fixation result, although, provided Mo and Ca are adequately supplied, greater acidity can be tolerated (Andrew 1978; Munns 1978).

2.2 Phosphorus

In discussing the effect of acidity on P status, it is important to invoke the distinction between desorption/solubility and availability. In many soils the level of P in solution is governed by reactions of the type presented in Table 1 and illustrated in Fig. 1. Above and below a pH value of about 5.5, P activity in solution is lowered as a result of reactions with solid surfaces. Much ambiguity has surrounded the effect of acidity on P availability which can largely be traced to neglect some of the factors involved. Lowering soil pH has been reported to decrease, increase or not affect soil P availability and uptake by plants (Haynes 1984; Sumner and Farina 1986). Raising soil pH above about 6, usually results in a decrease in P in solution and its availability due to the formation of insoluble Ca phosphates (White and Taylor 1977). Most published reports on solution P, its availability and uptake over the pH range in most soils conform to the patterns illustrated in Fig. 2 which, in turn, support the model in Fig. 1. However, there appear to be a few exceptions to this general trend which will now be discussed. A number of workers (Amarasiri and Olsen 1973; Munns and Fox 1976; Murrmann and Peech 1969) have demonstrated a decrease in soil solution P with increasing pH as illustrated in Fig. 3 even under strongly acid conditions. Haynes (1984) has pointed out that this behaviour probably results from the sorption of added P on newly precipitated hydroxy-Al surfaces. In several reported cases, P in solution passes through a minimum between pH 5.5 and 6.5 which coincides with the zone of minimum solubility of Al. Above about pH 6.5, solution P increases (Fig. 3) possibly due either to the formation of the $Al(OH)_4^-$ ion, which would then liberate the P previously sorbed, or to the increased rate of gibbsite crystallization as pH is raised progressively higher (Hsu 1977). Such a mechanism has been confirmed by Robarge and Corey (1979) working with an Al-saturated resin. This latter type of behaviour is likely to be only a transient feature of soils containing large amounts of soluble Al prior to liming. Several studies quoted by Haynes (1984) have shown that, with sufficient time and several cycles of wetting and drying, this pattern of behaviour is likely to disappear and revert to that illustrated in Figs. 1 and 2 as the hydroxy-Al polycations which initially sorb the added P recrystallize to form gibbsite. This view is supported by the work of Volkweiss (1973) who showed that the P sorption capacity of a soil limed to the point of Al neutralization was less after 3 months than 2 weeks of incubation. Thus given sufficient time to come to equilibrium, all soils are likely to follow the pattern illustrated in Fig. 1, although in the short term aberrant behaviour may be observed, particularly when lime and P are added simultaneously. Therefore in the absence of factors which might impair root performance such as soluble Al, there seems to be little evidence to support any view other than that the availability of P to plants is largely determined by equilibrium desorption/solubility considerations. Of course in some soils, capacity considerations may limit the rate of resupply to the soil solution thereby creating insufficiencies.

A substantial body of evidence has accumulated to show that roots, through their control of rhizosphere chemistry, can mobilize P for uptake by acidification

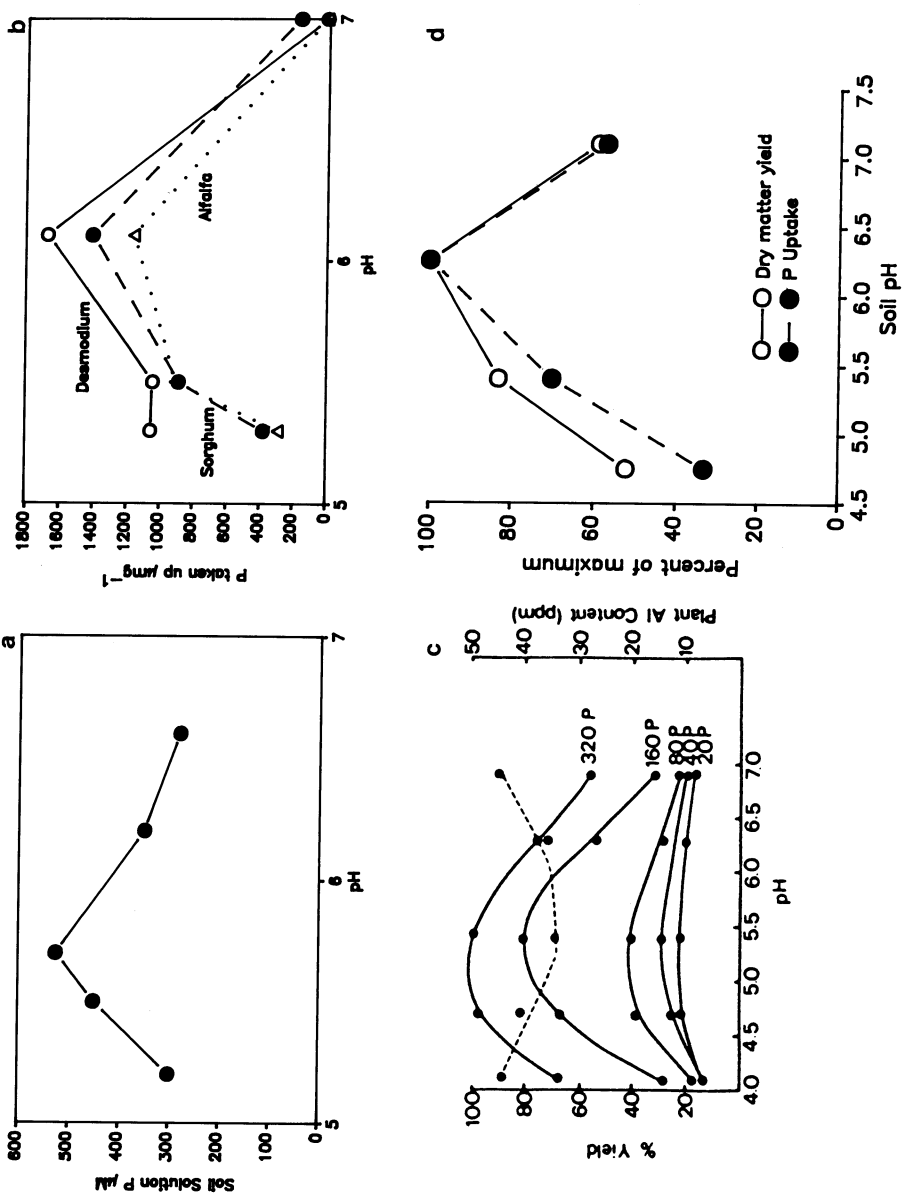

Fig. 2. Effect of pH on **a** soil solution P (plotted from data of Soltanpour et al. 1974); **b** P uptake (plotted from data of Fox et al. 1964); **c** maize yield (Sumner and Farina 1986); **d** maize dry matter yield and P uptake (Juo and Uzu 1977)

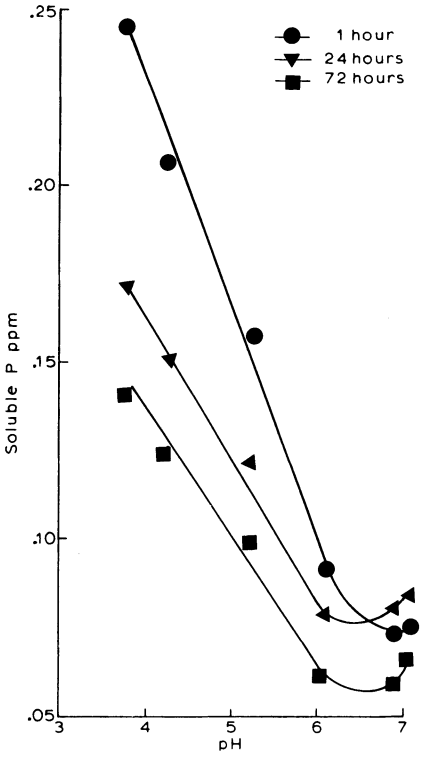

Fig. 3. Effect of shaking time on the relationship between pH and soluble P in an Oxisol (Amarasiri and Olsen 1973)

resulting from NH_4 rather than NO_3 uptake (Miller et al. 1970; Soon and Miller 1977; Sarkar and Wyn Jones 1982), by acidification resulting from N_2 fixation (Aguilar and van Diest 1981) and by acidification even when NO_3 is the only source of N (Grinsted et al. 1982). These reactions are likely to be effective in soils where apatites are the primary solid phase phosphates. In soils where solution P decreases with decreasing pH, Nye (1986) has suggested that if the rhizosphere pH were raised by excretion of HCO_3^-, P uptake might be increased although no proof is yet available.

2.3 Potassium

Soil solution K in acid soils is largely determined by reactions of the type presented in Table 1 as well as by the general exchange equation. Acid weathering liberates K from micaceous and felspathic minerals which would enter the soluble and exchangeable pools. However, in variable charge soils, increasing acidity results in decreasing CEC (Table 1) which would reduce the ability of the soil to retain K resulting in more in the soil solution as illustrated in Fig. 4. Thus solution K would then be prone to downward movement by leaching as illustrated in Fig. 5 which shows the ability of limed topsoil to retain

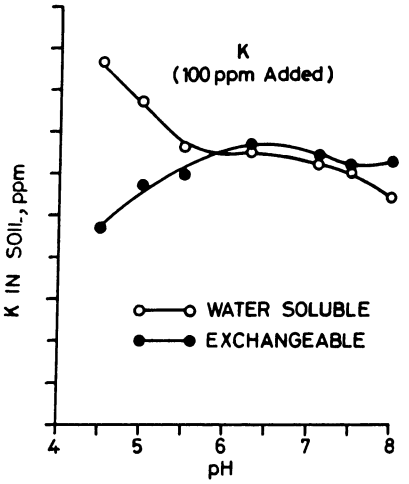

Fig. 4. Distribution of soluble and exchangeable K in a Nigerian Ultisol as a function of pH (Juo and Uzu 1977)

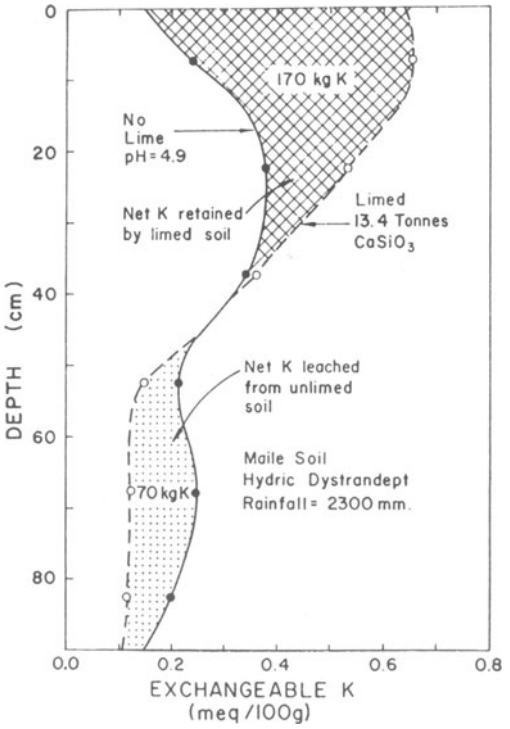

Fig. 5. The influence of liming on the distribution of exchangeable K in profiles of a Dystrandept in Hawaii. 100 kg K ha^{-1} is unaccounted for in the unlimed soil suggesting that it had been leached (Fox 1980)

additional K and of unlimed soil to lose K by leaching. Thus the more acid a soil becomes, the less K is likely to remain on exchange sites and in addition, increased levels of soluble Al (Table 1) would stunt the roots further exacerbating the reduced K supply to the plant. Excessive quantities of Ca and Mg can create imbalances with respect to K leading to problems of availability and uptake. The possibility of this picture being complicated by the possible occurrence of alunite $[KAl_3(OH)_6(SO_4)_2]$ in strongly acid soils is discussed in Section 4.1.

2.4 Calcium

The main equilibria determining the solubility of Ca in soils involve calcite, soil-Ca and simple cation exchange (Table 1). Under acid conditions the presence of calcite (lime) would only be transient and it would readily dissolve to give Ca^{2+} which would be held on exchange sites and in the soil solution. In acid soils, most of the Ca present would exist in soluble forms as Ca^{2+}. The soil-Ca line in Fig. 1 merely portrays the maximum solubility for Ca when in equilibrium with solid calcite surfaces. Unless soluble salts are present, the Ca activity in a soil solution in acid soils will always fall below this line. Changes in solution and exchangeable Ca with pH as a soil is limed are illustrated in Fig. 6 showing, as would be expected, that both increase with increasing pH value. Problems with Ca solubility or availability are seldom encountered in most soils although very acid soils and particularly subsoils may be deficient in Ca or deficiency may be induced as a result of high levels of soluble Al which reduce Ca uptake. Liming to neutralize exchangeable Al usually supplies adequate Ca

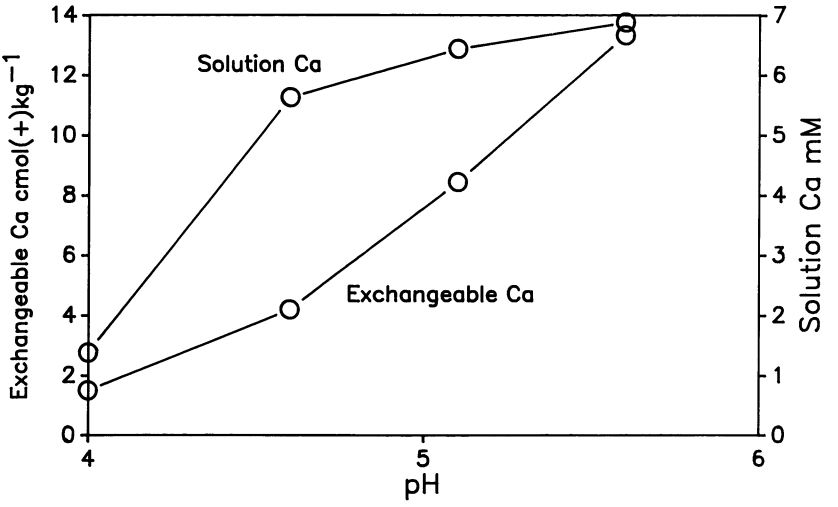

Fig. 6. Effect of pH on exchangeable and solution Ca on addition of $Ca(OH)_2$ to a New Zealand podzol (plotted from data of Haynes and Ludecke 1981)

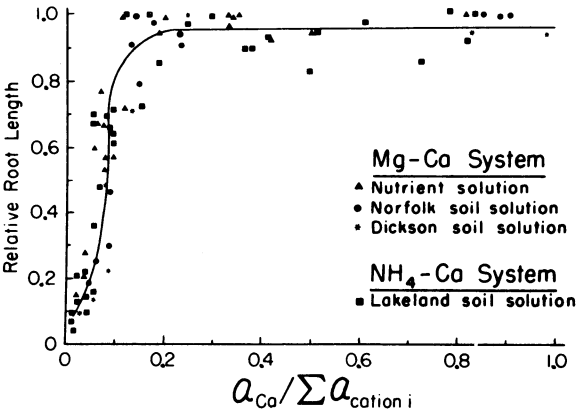

Fig. 7. Effect of the activity ratio of Ca/total cations in nutrient solutions and soil solutions in situ on growth rate of cotton taproots (Adams 1984)

for growth. Organic complexes are potentially a large repository for Ca when acid soils are limed, with the native Al being replaced by Ca. Further studies are necessary to determine the importance of these reactions. However, imbalances with Mg, NH_4 and K can create Ca availability problems under certain circumstances and Ca availability is then a function of the ratio of Ca to other cations in the soil solution (Fig. 7).

2.5 Magnesium

The solubility of Mg in acid soils is determined by that of dolomitic limestone, and Mg silicates such as vermiculite reflected by the Mg line in Fig. 1. Dolomitic limestone and Mg silicates are readily soluble under acid conditions and seldom would one encounter solubility problems at low pH values. Having dissolved (Table 1), the Mg enters exchange sites and some would remain in solution. The way in which Mg is distributed between these two forms when soil pH is varied using $Ca(OH)_2$ is illustrated in Fig. 8. As pH drops, less Mg is held in exchangeable form due to reduction in variable charge (Table 1) and more is present in solution available for loss by leaching. Magnesium is a poor competitor with Al and Ca for exchange sites and is often lost from the topsoil as a result of acidification (Fig. 9) or application of large quantities of soluble Ca. In addition, acidification reduces variable charge further aggravating the situation. Increasing CEC without Mg addition, reduces Mg saturation and such lime-induced Mg deficiencies can be quite striking (McNaught et al. 1973). As soil pH is raised to the vicinity of 5.5, Mg has been shown to precipitate possibly as a mixed Al, Mg double hydroxide or as a poorly ordered magnesian silicate rendering it less soluble and available to plants (Sumner et al. 1978).

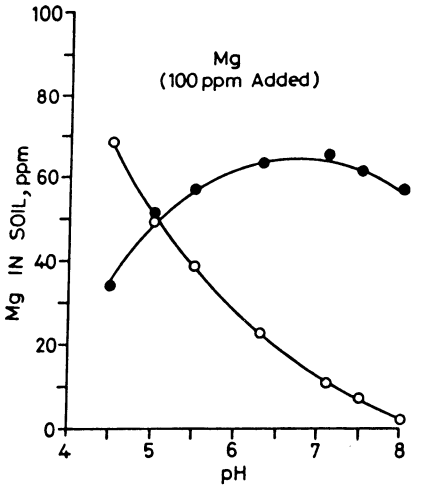

Fig. 8. Effect of pH on the distribution of soluble and exchangeable Mg in a Nigerian Oxisol (Juo and Uzu 1977)

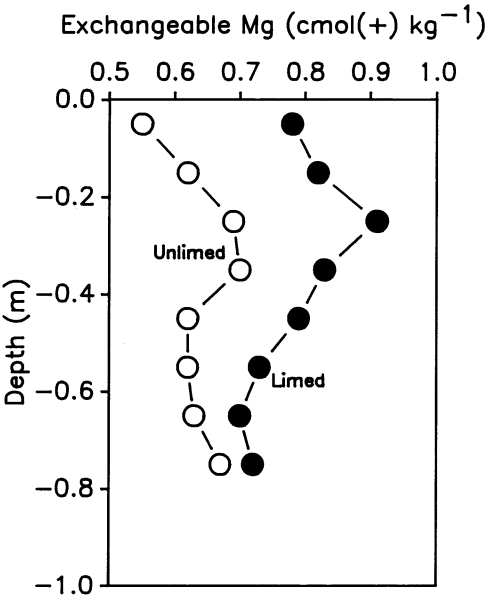

Fig. 9. Distribution of Mg with depth in a limed and unlimed Georgia Ultisol.

2.6 Sulphur

In many soils the main repository for S is in organic matter and its release is consequently dependent on biological transformations. In this regard, the reactions (Table 1) are essentially the same as for N with the exception that the parallel with nitrification is less sensitive to acidity and sulphate reduction

seldom takes place in most soils. In highly weathered acid soils, SO_4-S has been reported to be adsorbed by sesquioxidic surfaces (Chang and Thomas 1963), precipitated as an Al-OH-SO_4 type of mineral such as alunite or basaluminite (Adams and Rawajfih 1977) and/or held as a simple exchangeable anion on positively charged sites (AEC) on sesquioxides under acid conditions (Table 1). As the pH of such soils is raised, sulphate is released to the soil solution and becomes readily assimilable by crop roots as illustrated in Fig. 10. As the subsoils of most highly weathered soils are acid, they present a potential storehouse for S against leaching (Table 2) and provided roots are able to enter these zones, this S should contribute significantly to plant requirements. There is evidence that the interaction of K and SO_4 activities in soil solutions may be important under

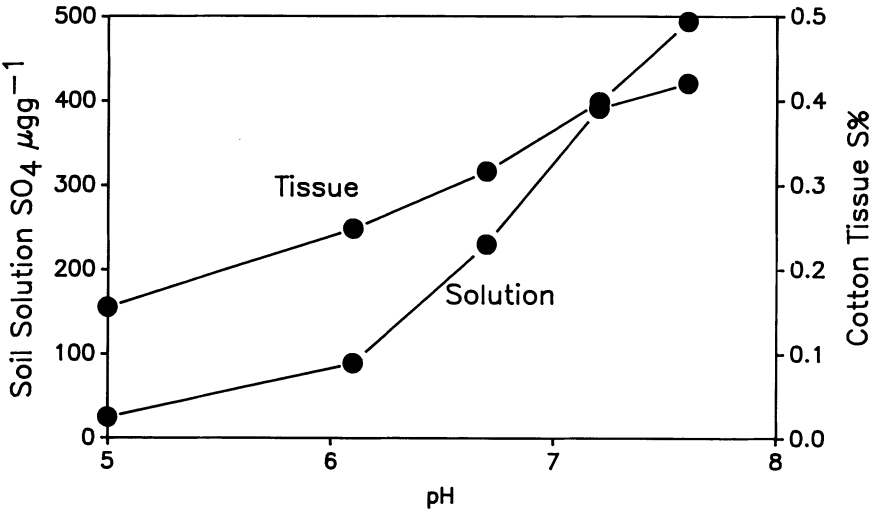

Fig. 10. Effect of pH on soil solution and cotton tissue sulphate from a Dothan soil limed to different pH values (plotted from data of Elkins and Ensminger 1971)

Table 2. Extractable sulphate-sulphur in variable charge soil profiles

Depth	Hawaii[a]		Nigeria[a]	Puerto Rico[a]	Georgia[b]
	Hydric Dystrandept	Typic Hydrandept	Oxic Paleustalf	Tropeptic Haplorthox	Typic Paleudult
m			gS g^{-1}		
0–0.15	150	220	25	414	196
0.15–0.30	320	1210	18	1036	396
0.30–0.60	830	3730	56	1271	472
0.60–0.90	950	5480	112	1260	354
0.90–1.20	960	4520	136	1225	326

[a] From Fox (1980).
[b] From Sumner et al. (1986).

acid conditions in forming insoluble solids, the implications of which will be considered in more detail later in this chapter.

2.7 Copper

In acid soil, copper occurs as Cu^{2+} in equilibrium with soil-Cu (Table 1 and Fig. 1) and its solubility increases with decreasing pH value. Copper is complexed strongly by organic matter with the result that most of the Cu in topsoils is organically bound in both insoluble and soluble complexes. In organic soils, Cu can be so strongly complexed as to reduce availability to deficient levels irrespective of pH value. Under acid conditions in non-organic soils, Cu seldom presents nutritional problems although on acid sandy soils deficiencies as a result of leaching losses of Cu are possible. Copper toxicities have been reported on acid soils receiving repeated applications of Cu pesticides (Spencer 1966).

2.8 Zinc

The level of soluble Zn^{2+} in soils is governed by the soil-Zn line in Fig. 1 which maintains a much lower level of Zn^{2+} than compounds such as $Zn(OH)_2$, $ZnCO_3$ and $ZnSiO_3$ (Lindsay 1972). Zinc activity increases rapidly with decreasing pH value which means that Zn nutritional problems are seldom encountered in soils at pH values below 5.5 provided they contain sufficient Zn. The pH-dependent solubility of Zn in soils appears to be governed by a complex mixture of mechanisms including adsorption on sesquioxides, co-precipitation with Al^{3+} and complexation with organic matter (Ellis and Knezek 1972; Grimme 1968; Stanton and Burger 1967). The availability of Zn follows the general pattern of solubility as presented in Fig. 1 although the effects of cultivars in differential uptake under the same conditions are often marked (Clark 1978; Paulsen and Rotimi 1968; Payne et al. 1986; Sumner et al. 1982). This pattern of behaviour is illustrated in Fig. 11.

2.9 Manganese

In addition to its solubility being determined by pH (Table 1), Mn is also very sensitive to changes in redox potential as illustrated in Fig. 1 where two lines have been plotted on the stability diagram for differing values of pH + pe. According to Lindsay (1979), this parameter is a simple single expression characterizing the redox status of soils with values greater than 16 representing moderate to extremely well-oxidized conditions. Thus the two lines for Mn^{2+} in equilibrium with pyrolusite were calculated using values for pH + pe of 16 and 20. Most agricultural soils should fall within this zone. The effect of redox conditions is therefore potentially much greater than that of acidity in determining the level of soluble Mn in soils. Nevertheless at any given redox state,

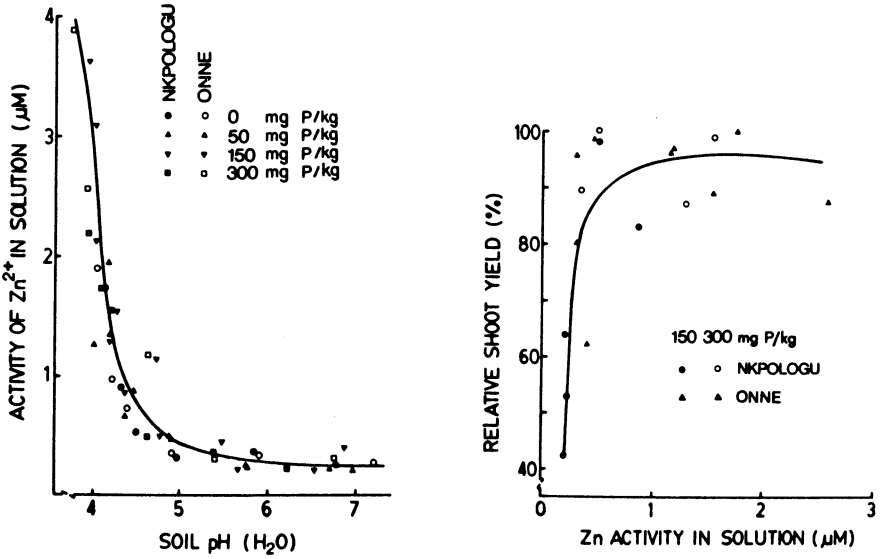

Fig. 11. Effect of pH on Zn^{2+} activity in soil solution and its effect on relative shoot yield of maize grown in two Nigerian Ultisols differently fertilized with lime and P (Friesen et al. 1980a,b)

decreasing pH results in increased levels of soluble Mn. Except in rare cases, where soils are totally deficient in Mn, nutritional problems involving Mn solubility under acid soil conditions are seldom encountered. If anything, Mn is more likely to be present in toxic quantities under such conditions particularly if pH + pe is much less than 20 under which conditions Mn^{2+} could be considered as a macro- rather than micronutrient. In many soils, Mn toxicity may be more important than Al toxicity in limiting crop production. The pH required to bring the solubility of Mn to a low level is higher than that for Al (Fig. 12). The relationship between pH, exchangeable Mn and growth of tomatoes is illustrated in Figs. 12 and 13. A depressive effect of high levels of Mn on growth is apparent below a pH value of about 5.8 at which point the solubility of Mn increases markedly with decreasing pH. Of the order of 11–13 mg Mn l^{-1} of soil solution have been shown to induce toxicity symptoms in sensitive crops (Adams and Wear 1957; Morris 1949). Thus below pH values of about 6, Mn can be expected to become soluble in toxic quantities which can adversely affect the growth of sensitive crops. These toxic levels of Mn can be reduced by the addition of organic matter through chelation (Foy 1984) and by some microorganisms that can oxidize divalent Mn to the insoluble tetravalent state (Bromfield 1979).

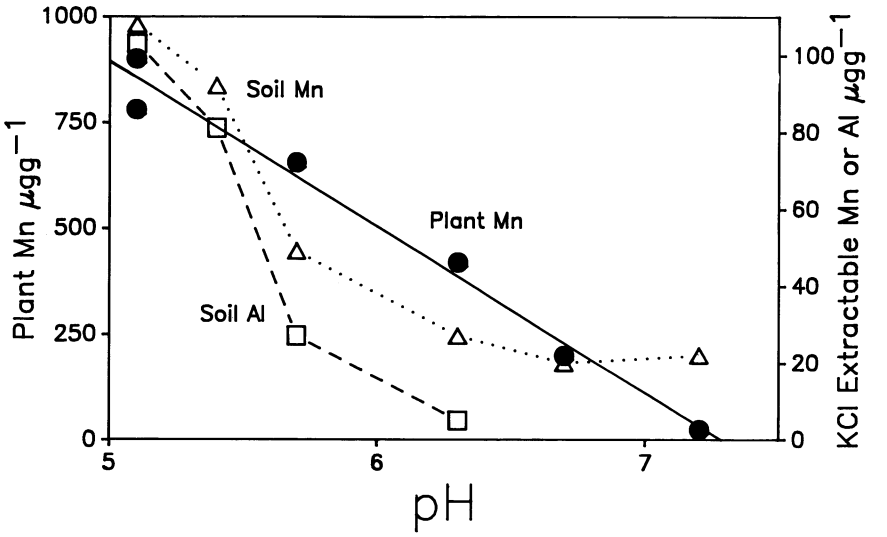

Fig. 12. Effect of soil pH on exchangeable Al and Mn and plant Mn for tomatoes grown on Wahiawa soil (plotted from data of Jones and Fox 1978)

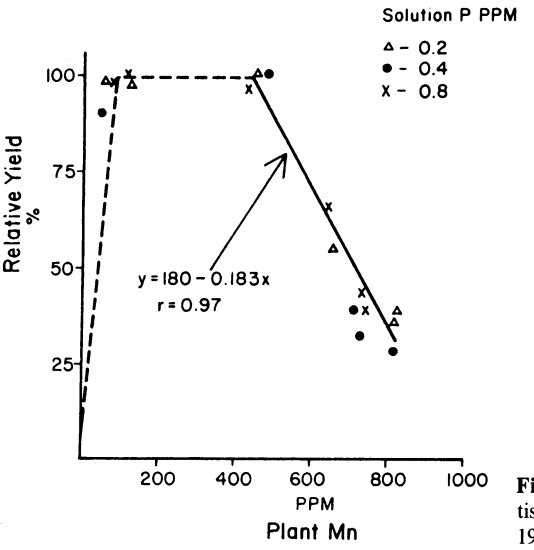

Fig. 13. Effect of Mn content of tomato tissue on relative yield (Jones and Fox 1978)

2.10 Iron

Iron solubility in soils follows a similar pattern to that discussed above for Mn, although the effect of redox is much less and the overall solubility of Fe^{3+} is much less than that of Mn^{2+} (Table 1, Fig. 1). Thus, one can expect that few problems of Fe toxicity will ever be encountered in soils with pH + pe values above 16. Because of the very low solubility of Fe even under very acid conditions, redox reactions are likely to be of great importance in the rhizosphere in solubilizing sufficient Fe for the needs of a crop. This has been demonstrated by Gardner et al. (1982) and Römheld et al. (1982) who have shown that acid and reducing agents excreted by root tips solubilize Fe, Mn and Zn thereby increasing their uptake. Most problems with Fe nutrition are encountered when pH is raised by liming resulting in a sufficient depression of Fe solubility to induce deficiency in crops unable to engage compensatory mechanisms in their rhizospheres.

2.11 Boron

In the pH range of acid soils, B occurs in solution as the uncharged H_3BO_3 molecule and is strongly adsorbed by soils containing sesquioxides, organic matter and soluble Al as the pH is raised (Table 1). This is illustrated in Fig. 14. This B adsorption results in exchange of OH or water molecules on the surface with consequent strong bonding with little desorption by leaching particularly at higher pH values (Rhoades et al. 1970). Thus B availability in soils would increase with decreasing pH as illustrated in Fig. 15. Provided adequate B has

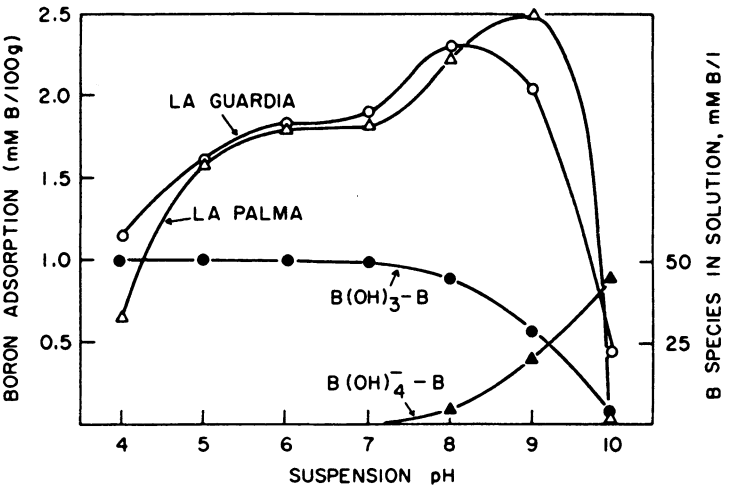

Fig. 14. Effect of pH on boron adsorption and in solutions for two soils (Bingham et al. 1971)

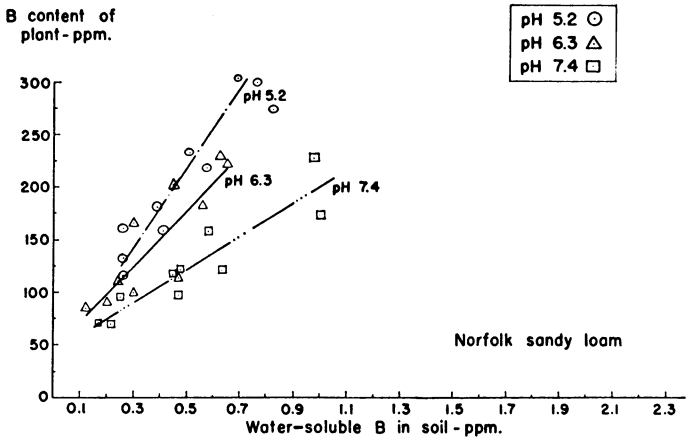

Fig. 15. Relationship of water-soluble soil boron to plant B content at three pH levels on a Norfolk soil (Wear and Patterson 1962)

been applied few problems would be anticipated in terms of availability in most acid soils.

2.12 Molybdenum

The problem of Mo availability to plants growing in acid soils is compounded by the fact that it is both a trace element (usually < 5 ppm upon total analysis) and highly insoluble in acid soils. Very often its availability is assured simply by liming, although sometimes Mo must be added to rectify deficiencies (often the treatment of seed or simply the selection of seed grown on soils with adequate Mo supply is all that is required to avoid Mo deficiency).

The pH-dependent solubility of Mo is difficult to establish quantitatively (hence the estimate for "soil-Mo" provided by Vlek and Lindsay 1977 and shown in Fig. 1), although a likely candidate suggested by Krauskopf (1972) is ferrimolybdite $[Fe_2(MoO_4)_3 \cdot 8H_2O]$ with a pK_{sp} value of about 52.

In coming to terms with Mo-deficiency problems, the development of routine soil tests for Mo (Karimian and Cox 1978) is likely to be less successful than approaches such as that of Franco and Munns (1981) which recognize the potential for manipulating, both genetically and environmentally, the level of Mo in seed.

2.13 Silicon

Of the several elements, other than those already discussed, for which there is at least some evidence for a beneficial effect on plant growth, Si is perhaps the most

deserving of mention in relation to acid soils. Soil acidity which has developed naturally through leaching and weathering is typically associated with a mineral assemblage having a low silica:sesquioxide ratio. As a result, levels of silica in the solution of acid soils may commonly be an order or more of magnitude lower than in the solution of less weathered (and inherently more fertile) soils.

Iler (1979) has reviewed extensive literature dealing with the direct and indirect benefits of silica on the growth of plants. A classical example of silica effects on crops is with sugarcane on Oxisols (Fox et al. 1967) (Fig. 16). In many such cases, the effect is probably only partially related directly to Si uptake. At least part of the interest in silica application to acid soils stems from the potential for competition between silicate and phosphate for desorption sites (Obihara and Russell 1972), which suggests itself as a mechanism for the widely observed enhancement of P in solution after Si application to soil (Smyth and Sanchez 1980).

Silica may, of course, have other benefits, such as the reduction of Al toxicity through co-precipitation. Recent work in our laboratories has also shown a positive effect of Si on root length of soybeans grown in nutrient culture solutions which is apparently unrelated to shoot growth and manifests itself even in the absence of Al. Apart, then, from any direct benefits derived through plant uptake, Si may be viewed as an element which favourably tempers both the nutritional environment of plant roots as well as their ability to respond to it. In practice, Si would most frequently be applied to soils as an alkaline slag in which calcium silicate would be the dominant compound (Tisdale et al. 1985). In such cases the roles of Ca, alkalinity and other plant nutrients present as impurities may be difficult to resolve from that of Si. The results of field experiments should be interpreted accordingly.

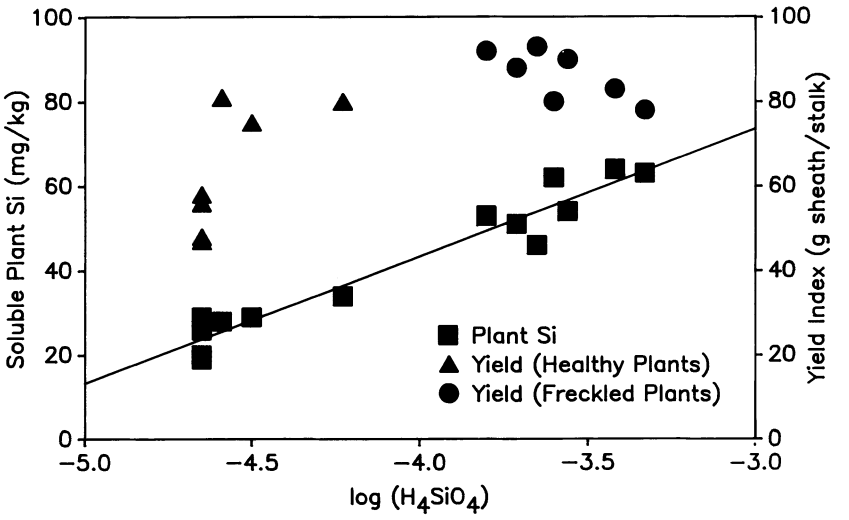

Fig. 16. Relationship between water-soluble Si and plant Si, growth and freckling disease incidence for sugarcane on Hawaiian soils (After Fox et al. 1967)

3 Toxicity Problems in Acid Soils

Enhanced solubility of certain metal cations is an important consequence of soil acidification. The resulting toxicity of those elements which are essential to plant growth (Mn being the most important) appears to be due primarily to a nutrient imbalance brought about by abnormal accumulation in plant tissue. By contrast, the effect of Al toxicity appears to be largely manifested as a pronounced malformation as well as malfunction of the root system (Foy 1984; Bennet et al. 1986), a syndrome which is exacerbated by low levels of soil Ca. Kamprath (1984) has presented a useful perspective of the various toxicity factors influencing plant growth on acid soils, and this section is intended to supplement his review with some further observations based on current research in this field.

3.1 Manganese Toxicity

Mn toxicity is not as predictable as Al toxicity in acid soils. Part of the problem lies in the fact that Mn solubility depends upon the redox parameter (pH + pe), and not simply pH alone. Aside from this aspect, it would appear that many, possibly even the majority, of naturally acid soils have rather low levels of exchangeable Mn, probably as a result of leaching under acid conditions. Accordingly, one might expect Mn toxicity problems to be far more frequent on those soils in which acidity has only developed following intensive crop cultivation and fertilization (A.D. Manson 1986, pers. commun.). At the very least, the possibility for recognizing Mn toxicity on strongly acid soils is likely to be masked by the prevalence of Al toxicity.

3.2 Al Toxicity in Relation to Ca Level and pH

With the use of $CaCO_3$ or $Ca(OH)_2$ for liming acid soils, the simultaneous correction of Al, Ca and acidity towards more favourable levels follows automatically. The increasing use of exchangeable (usually measured as *M* KCl-extractable) Al as a criterion for estimating lime requirement, especially on soils of the humid tropics (Kamprath 1984), should be viewed more as an empirical expedient than a theoretical necessity. Useful calibrations do not necessarily reflect causal relationships, and it may simply be fortuitous that the amount of lime needed to reduce the calculated Al saturation of effective CEC to a particular level corresponds well with the economic optimum established for certain soil types by field experimentation. The desirable reduction of Al level varies in any case with crop species and even cultivar (Foy 1984).

There is evidence to indicate that the high levels of Al which dissolve from acid soils shaken with concentrated electrolyte solutions are no higher than would be predicted on the basis of an assumed equilibrium with solid phase species such as gibbsite or kaolinite after correcting for both ionic strength effects and the formation of ion pairs such as $AlCl^{2+}$. This indicates that the level of KCl-extractable Al will depend on the most soluble solid phase present and

on pH, but not necessarily on the magnitude of CEC or its supposed degree of saturation with Al. Even the sequential extraction method of Skeen and Sumner (1965), which corrects for constant background dissolution of solid phase Al, may not necessarily reflect exchangeable Al in the Coulombically-adsorbed sense as is normally used in reference to alkali and alkali-earth cations. These circumstances suggest that terms such as "exchangeable Al" and "Al saturation of (effective) CEC" should be dropped from the soil acidity and liming vocabulary.

None of this detracts from the fact that Al, Ca and H ion concentrations have all been shown to independently influence the growth and performance of plant roots. From the literature available (Kamprath 1984), it seems probable that the effects of these three ions interact in a complex manner (e.g. increasing Ca level ameliorates the effect of a particular Al and/or pH level) which is best observed if plants are grown in nutrient solution media and if relative activities of the ions are considered as opposed to their concentrations. Some examples of the success of this approach are discussed in Section 4.

3.3 Al Toxicity and Soil Organic Matter

The toxicity of a particular concentration of Al in solution appears to be reduced considerably when the Al is complexed by organic compounds (Fig. 17; Bartlett and Riego 1972; Hue et al. 1986). The level of extractable or soluble Al which can be expected at a particular pH level also appears to be modified by the presence of solid phase, organic-Al complexes (Bloom et al. 1979). Judicious

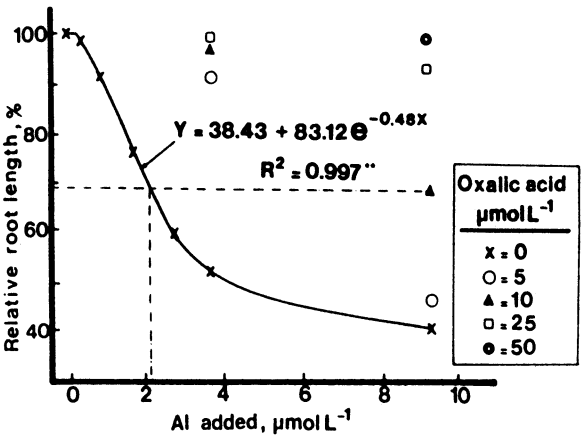

Fig. 17. Relative root length as a function of initial concentrations of $AlCl_3$ and oxalic acid. *Solid line* presents Al effect in the absence of organic acid (standard curve for Al toxicity). *Dashed line* illustrates conversion of root growth in the presence of oxalic acid to equivalent monomeric Al concentration, e.g., 68% relative root growth with 10 μmol l^{-1} oxalate + 9.25 μmol Al l^{-1} is equivalent to 2.2 μmol Al l^{-1} in the absence of oxalate (Hue et al. 1986)

management of soil organic matter levels in acid, highly weathered soils is already recommended for maintaining CEC and enhanced P availability. The effect of liming on the stability of both soluble and insoluble organic-Al complexes still needs to be investigated.

3.4 Al Toxicity, Soil Solution Ionic Strength, and the Effect of Soil Drying Cycles

The addition of fertilizer to highly leached acid soils might be expected to raise soil solution ionic strength, with the potential for pH reduction and enhancement of Al solubility. Friesen et al. (1980a) have shown that this effect can be quite considerable (Table 3). Whether one invokes the Ratio Law or simply a consideration of solubility equilibria of sparingly soluble solids, it can be predicted that ionic strength enhancement will give rise to increased levels of soluble Al even without the necessity of a concomitant decrease in pH. This principle can be extended to include the effect of intermittent soil drying on the expression of Al toxicity, and its consideration could be important in the evaluation of both glasshouse trials (in which watering practices typically are designed to avoid water stress) as well as field experiments where seasonal soil water variations may confound the results. The implication here is that not only does Al reduce crop tolerance to water stress through root damage, but also that the conditions of water stress, which will give rise to concentration of electrolyte in the soil solution, will intensify Al toxicity.

Table 3. Effect of basal fertilizer on pH and exchangeable and soluble Al in soils without lime or phosphate applied (Friesen et al. 1980a)

Treatment	Soil pH	Exchangeable Al	Exchangeable Al saturation	Soluble Al
		meg/100 g	%	μg/ml
		Nkpologu soil		
Without fertilizer	4.72	1.88	63.9	0.6
With fertilizer	4.16	1.28	41.8	11.1
		Onne soil		
Without fertilizer	4.32	1.79	59.7	2.7
With fertilizer	4.07	1.41	45.0	10.2

4 Ion Activities in the Soil Solution: An Alternative Perspective to Soil Acidity Problems

Judging from a recent review by Soon (1985), what one might term the mainstream view of the concept of soil nutrient availability underwent a clear change of direction from an earlier, predominantly pre-1960's approach, which

attempted an understanding of availability within a well-defined physico-chemical framework [exemplified by the papers of Schofield (1955), Clark and Peech (1955) and Beckett (1964)], to a somewhat more phenomenological approach emerging from the scepticism which accompanied failed attempts, such as that of Larsen and Court (1960), to demonstrate the independence of chemical potentials upon soil:solution ratio and ionic strength. With the benefit of hindsight it is usually easy to identify the additional variables in these earlier experiments of which the authors were unaware (such as ion pair formation and interference by exchangeable cations in Larsen and Court's study), and therefore to conclude that such scepticism was unjustified. An unfortunate result, however, has been the appearance in the last two to three decades of a plethora of empirical studies, including measurement and best-fit modelling of adsorption-desorption phenomena, which are conspicuous for their failure to make any use whatsoever of either single-ion activities or chemical potentials as a basis for the correlation of results, either within or between different experiments.

Soon (1985) has rationalized the popularity of using concentration rather than activity ratio or product as a measure of the intensity factor by suggesting that it is ion concentrations, and not activities, to which plants will respond. This assumption might be reasonable in the case of elements for which mass-flow transport predominates and towards which roots exhibit no preference or selectivity; it would not be expected to hold for nutrients the mobility of which is diffusion-limited and/or the uptake of which is subject to the operation of a carrier mechanism (da Silva and Williams 1976). In vindication of this view, Salmon (1964) found a strong correlation between the Mg concentration in grass and a Mg activity ratio including Ca, K and H in soil solution, while Sposito (1984) has reviewed more recent data showing the strong correlation of leaf metal concentration (Al, Cd) with the activity of the corresponding free ion in nutrient solutions. An example of the importance of Ca activity relative to that of total cations in governing root growth has already been discussed (Adams 1974; Fig. 7).

Increasing use is now being made of approaches which involve a consideration of ionic activities and chemical potentials in soil solutions. This has been made possible by (1) advances in laboratory techniques, both for extracting soil solutions (Wolt and Graveel 1986; Elkhatib et al. 1986) and for convenient semi-micro, multi-element analysis of solutions by methods such as ion chromatography and plasma spectroscopy; (2) a greatly expanded base of critically compiled thermodynamic data [Sposito (1986) lists a number of sources]; and (3) the increasing sophistication as well as accessibility of ion-association models (Amacher 1984; Baham 1984; Sposito 1984, 1986) which make possible a comprehensive prediction of solution equilibrium states compared with approaches (e.g. Adams 1974; Lindsay 1979) which, while usefully illustrating the principles involved, have tended to oversimplify the conditions pertaining to a particular element in solution.

A major advantage of considering both nutrient availability and toxicity problems in acid soils in terms of ion activities and particularly activity products

(i.e. chemical potentials) lies in the possibility of relating plant performance directly to the nature of the solid phase in equilibrium (assuming that this is at least closely attained) with the soil solution. The remainder of this chapter will focus on some recent studies which illustrate the applicability of this approach.

4.1 Relationship of Nutrient Uptake to Chemical Potentials

Attempts to describe nutrient availability in terms of an intensity factor, represented by activity ratios such as $a_K/a_{(Ca+Mg)}^{1/2}$ [the Potassium Potential of Beckett (1964)], have met with varying success. The example cited earlier dealing with Mg (Salmon 1964) is a case in point. Salmon found that % Mg in grass was best described ($r = 0.95$) by the activity ratio expression: $a_{Mg}^{1/2}/a_{(Ca+Mg)}^{1/2} + B \cdot a_K + C \cdot a_H$ in which a is the solution activity of the indicated ion and B and C are coefficients. The partial empiricism of such expressions is understandable given the assumption that other cations (e.g. Al^{3+}, NH_4^+, Na^+) are present in negligible amounts and that the anion status of the soil solution remains constant relative to cations over the range of conditions pertaining to the experiment.

As an illustration of how inadequate the conventional expression $a_K/a_{(Ca+Mg)}^{1/2}$ may be as a measure of K potential, Table 4 shows the variation in a number of parameters for a group of soils selected on the basis of their solutions having an alunite potential within the range of 83.4 to 85.6 reported for the alunite solubility product by Nordstrom (1982). Only 8 of these 24 soils had such alunite potentials without the inducement of KNO_3 or $CaSO_4 \cdot 2H_2O$ application before equilibration at field capacity for 2 months. The significance of an alunite potential within the range indicated lies in the evidence (not proof) which it provides for the possible existence of alunite as a solid phase in equilibrium with the soil solution. It is important to note that the alunite potentials of 17 of these 24 soils only shifted into the range suggestive of alunite equilibrium (from a prior condition of undersaturation) after addition of KNO_3 and/or gypsum. In this respect it was also found that K addition generally reduced both the concentration and activity of SO_4 in solution and vice versa. Where this was not the case, soluble Al and/or pH shifts were consistent with alunite precipitation. Recognizing the possible existence of such equilibria may help to overcome one of the major difficulties in using the nutrient potential concept, namely, a suitable choice of co-ion or counter-ion (Oertli 1973). This is not to suggest that the alunite potential in the above example would alone be a satisfactory expression for K potential from the point of view of K availability. No doubt a more extended expression incorporating Ca and Mg (as competing ions for root absorption) would have a better chance of being meaningful. The above example also illustrates the value of the chemical potential (as opposed to single ion activities) as a basis for formulating hypotheses about causal relationships which otherwise might remain concealed. For example, might the formation of alunite help to explain apparent K fixation which is occasionally reported in acid, kaolinitic soils for which the usual explanation involving

Table 4. Selected single-ion activities and chemical potentials for soil solutions extracted from various Ultisols incubated with KNO_3 and/or gypsum for 2 months (Fey et al. 1986)

	pH	pK^+	pAl^{3+}	pSO_4^{2-}	pH-1/2pCa	pH-1/3pAl	pK-1/2p (Ca + Mg)	p(Alunite)[a]
	5.32	1.85	8.28	2.50	4.19	2.56	0.78	83.8
T	4.10	2.44	4.76	4.41	2.69	2.51	1.23	85.0
O	5.08	3.68	6.45	3.53	3.54	2.93	2.21	83.6
P	5.94	3.21	8.07	4.09	4.55	3.25	1.90	84.0
S	5.90	2.91	8.17	4.17	4.60	3.18	1.70	84.4
O	5.78	2.94	7.86	4.29	4.44	3.16	1.69	84.4
I	5.58	2.51	7.37	4.42	4.34	3.12	1.36	84.0
L	3.98	3.30	4.35	4.50	2.60	2.53	2.01	85.5
S	3.88	2.46	3.97	4.39	2.55	2.56	1.22	83.9
	4.68	2.94	5.92	3.55	3.06	2.71	1.41	83.7
	4.28	3.11	6.13	2.78	2.96	2.24	1.87	85.4
	5.57	2.19	8.00	3.88	4.27	2.90	0.94	84.5
S	5.32	4.22	6.92	4.15	3.85	3.01	3.17	85.3
U	5.41	4.60	7.66	2.61	4.12	2.86	3.37	84.3
B	5.44	3.73	7.20	3.74	3.68	3.04	2.02	84.2
S	5.15	3.82	7.71	2.67	3.91	2.58	2.62	85.4
O	5.94	3.63	8.17	2.78	4.27	3.22	2.05	84.4
I	5.75	3.29	7.89	4.07	4.32	3.12	1.96	84.6
L	5.81	5.08	8.16	2.60	4.53	3.09	3.86	83.9
S	4.72	3.36	6.01	3.65	2.76	2.72	1.45	84.4
	5.26	3.17	7.68	2.68	4.01	2.70	1.98	84.0
	4.21	2.36	4.64	4.98	2.53	2.66	0.88	85.0
	4.71	3.56	6.38	2.66	3.38	2.58	2.25	83.8
	4.70	3.09	6.27	3.81	3.12	2.61	1.57	85.3

[a] $pK + 3pAl + 6pOH + 2pSO_4$.

vermiculitic mineralogy does not apply?; Is Ca antagonism towards K uptake by plants, resulting from gypsum application, solely due to competition by Ca for absorption by roots, or is the precipitation of alunite involved?; Is the availability of K different when applied to acid soils as K_2SO_4, KCl or KNO_3?; where the inclusion of Al^{3+} activity in the K activity ratio expression provides a better prediction of crop yield response on acid soils (Tinker 1964), is this because of control of solution Al and K activities by alunite in the solid phase? Questions such as these might not have arisen without an examination of the data for indications of possible solid phases which might be in equilibrium with the soil solution.

This case history is incomplete in that it neither includes correlation with plant nutrient uptake data, nor does it address the question of nutrient supplying power, involving both the quantities held in the solid phase as well as rates of nutrient migration into and through solution. It does, however, provide some fresh insights on the nutrient potential concept. Taken together with the earlier discussion of pH-dependent phosphate availability, which pointed to the probability of a strong mediating influence by solubility equilibria, there would

seem to be strong enough grounds for re-examining chemical potentials of plant nutrients in soil solutions, especially in view of the more comprehensive and convenient manner in which this can now be achieved.

4.2 Chemical Potentials and Root Response to Ca and Al

4.2.1 Solid Phase Control of Al Solubility

Evidence was cited earlier which called into question the concept of exchangeable Al, or at least its operational definition as Al extractable in concentrated unbuffered electrolyte solution. The fact that equilibrium solubility for gibbsite has been shown to be attainable within 2 h (May et al. 1979) further suggests that solid phase dissolution may be the overriding factor controlling Al levels in soil solutions. Nordstrom and Ball (1986) have presented data for acid drainage waters which strongly suggested equilibrium with a microcrystalline gibbsite-like phase (Al basicity of 3) for pH values above 4.6, and probable control of solution Al activity by a basic aluminum sulphate mineral (apparent Al basicity of 1.7) below pH 4.6.

That this picture of Al solubility equilibria may be somewhat simplistic is evident from Fig. 18, which depicts the possibility of two other mineral assemblages giving an identical pH-dependence of Al activity to that of gibbsite. Kaolinite-halloysite control of Al solubility would depend on crystallinity as well as the activity of soluble Si (in Fig. 18 the latter is fixed by assuming equilibrium with quartz).

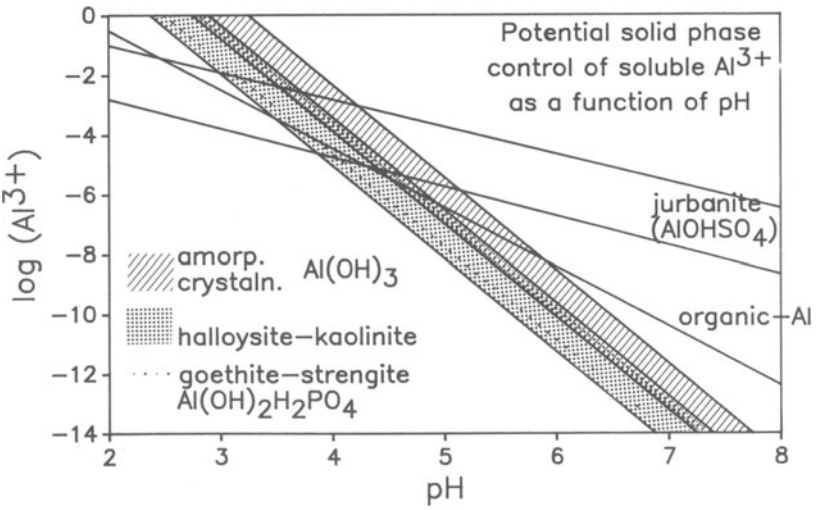

Fig. 18. Dependence of Al^{3+} activity upon solution pH in equilibrium with various mineral phases (organic Al line based on Mardin sample of Bloom et al. 1979; jurbanite pK_{SO_4} taken as 27.8 after Nordstrom 1982)

The $Al(OH)_2H_2PO_4$ phase would appear to be a likely reaction product between Al and P on the basis of a good deal of corroborative evidence (Traina et al. 1986). Figure 18 shows the effect which an equilibrium conceived between goethite, strengite and $Al(OH)_2H_2PO_4$ would have on the pH-functional solubility of Al. A decrease in goethite crystallinity would shift the $Al(OH)_2H_2PO_4$ line upwards to a position above the amorphous $Al(OH)_3$ line in the limiting case of Fe being completely amorphous. Interestingly, the imposed equilibrium with goethite and strengite yields the same pAl/pH slope for $Al(OH)_2H_2PO_4$ as that for gibbsite, a result which is not readily apparent from stoichiometry. Depending on crystallinity of the phases considered as well as factors such as Si activity, Fig. 18 illustrates the possibility of a pAl-pH relationship defining all the solid phases simultaneously, and coinciding approximately with the solubility of a moderately crystalline gibbsite.

The jurbanite and organic-Al solubility lines have been included in Fig. 18 to illustrate alternative possibilities for the shallower pAl/pH slope, under strongly acid conditions, reported by Nordstrom and Ball (1986). The dependence of the jurbanite line's intercept upon sulphate activity (the same would also apply for other basic aluminium sulphate minerals) might provide an explanation for the anomalous slope pertaining to Nordstrom and Ball's data, since sulphate activity might be expected to increase with increasing acidity of mine drainage waters. Alternatively, it may be noted that both the slope and intercept of the organic-Al line vary with degree of saturation of organic functional groups by Al (Bloom et al. 1979), making such a phase potentially the most stable form of solid phase Al under strongly acid conditions.

4.2.2 The Effect of Al and Ca on Root Growth

The importance of relative Ca activity on root growth has been mentioned. The ameliorative effect of Ca on Al toxicity is well known (Foy 1984).

Despite a good deal of recent work aimed at identifying the solution conditions, and especially Al activity levels, which are critical for root development (Pavan et al. 1982; Blamey et al. 1983; Alva et al. 1986a,b; Hue et al. 1986; Kim et al. 1985), there would still appear to be a need for some form of expression which simultaneously accounts for the effects of Al and Ca. Adams' (1974) ratio of $a_{Ca^{2+}}$ to $\Sigma a_{cations}$ (Fig. 7) is essentially an expression for the chemical potential of Ca, except that it ignores cation valence. Specific expressions have been formulated in which the activities of Ca, Al and valency are considered simultaneously. These ratios

$$(a_{Ca^{2+}})^{1/2} / (a_{Al^{3+}})^{1/3}$$

or

$$1/2\log a_{Ca^{2+}} - 1/3\log a_{Al^{3+}}$$

have been successfully used as a discriminant of soil solution conditions corresponding to gypsum-induced yield responses by maize (Buyeye et al. 1985) and lucerne (Sumner et al. 1986). The previous two equations assume that the

activity of Al^{3+} is the dominant species resulting in the expression of toxicity in plants. Recent evidence suggests that other monomeric Al species, i.e. $AlOH^{2+}$, $Al(OH)_2^+$, are just as detrimental to root growth in a number of plant species (Alva et al. 1986a,b; Cameron et al. 1986). Recently, Noble et al. (1988) confirmed the usefulness of an expression including the various monomeric Al forms in a study on soybean root growth in nutrient culture solutions containing a wide range of Ca and Al levels. Figure 19a,b shows clearly the suppressive effect of monomeric Al^{3+} and $AlOH^{2+}$ on root growth. However, a plot of the activity of Al^{3+} on a semi-log scale (Fig. 19c) gives a much better indication of the variation due to Ca at non-inhibitory levels of Al, which would suggest that under the prevailing solution conditions both Ca and Al play a role in determining root growth. An expression termed CAB (calcium-aluminium balance) which incorporates the various Al and Ca monomeric species in the system resulted in a better fit of the data (Fig. 19d):

$$CAB = 2\log(Ca^{2+}) - \{3\log(Al^{3+}) + 2\log(AlOH^{2+}) + \log[Al(OH)_2^+]\}$$

Thus as the equivalent activity of Ca becomes less than that of Al (values of CAB decrease in Fig. 19d), optimal root development can no longer be expected. Variants of the CAB expression (involving a consideration of ionic potentials of other basic cations beside Ca, and of the activity of total monomeric species in solution as opposed to the free metal ion) have not been found to enhance its predictive capacity (Noble et al. 1988). The significance of such an expression is further borne out when considering the uptake of Ca by the plant. In a similar nutrient solution experiment (Noble and Sumner 1988), soybeans were grown for 21 days after which the nutrient composition of the tops was determined. A plot of the activity of Ca^{2+} in solution against Ca uptake of the shoots shows three distinct curves depending on the level of Al in solution (Fig. 20a). When the same set of data was plotted against CAB, a single hyperbolic function was able to explain Ca uptake, thereby suggesting the interactive effect of various monomeric Ca and Al species on the uptake of Ca by the plant.

5 Concluding Remarks

The treatment of nutrient status and toxicity problems of acid soils in this chapter has largely followed a simple model based on known solubility equilibria involving solid phases of the elements under consideration. In some respects this may have oversimplified the picture, but the advantages of such an approach are quite demonstrable in terms of plant response correlations (the data reviewed here for P nutrition being perhaps the best example) and may become even more apparent if the concept of chemical potential is incorporated in the approach. Chemical potentials can have meaning both as parameters of plant biochemistry and as a geochemical reflection of soil mineral composition and buffering. To the extent that a chemical potential has a built-in pH term and also that it is independent of ionic strength, it will be less sensitive to sharp

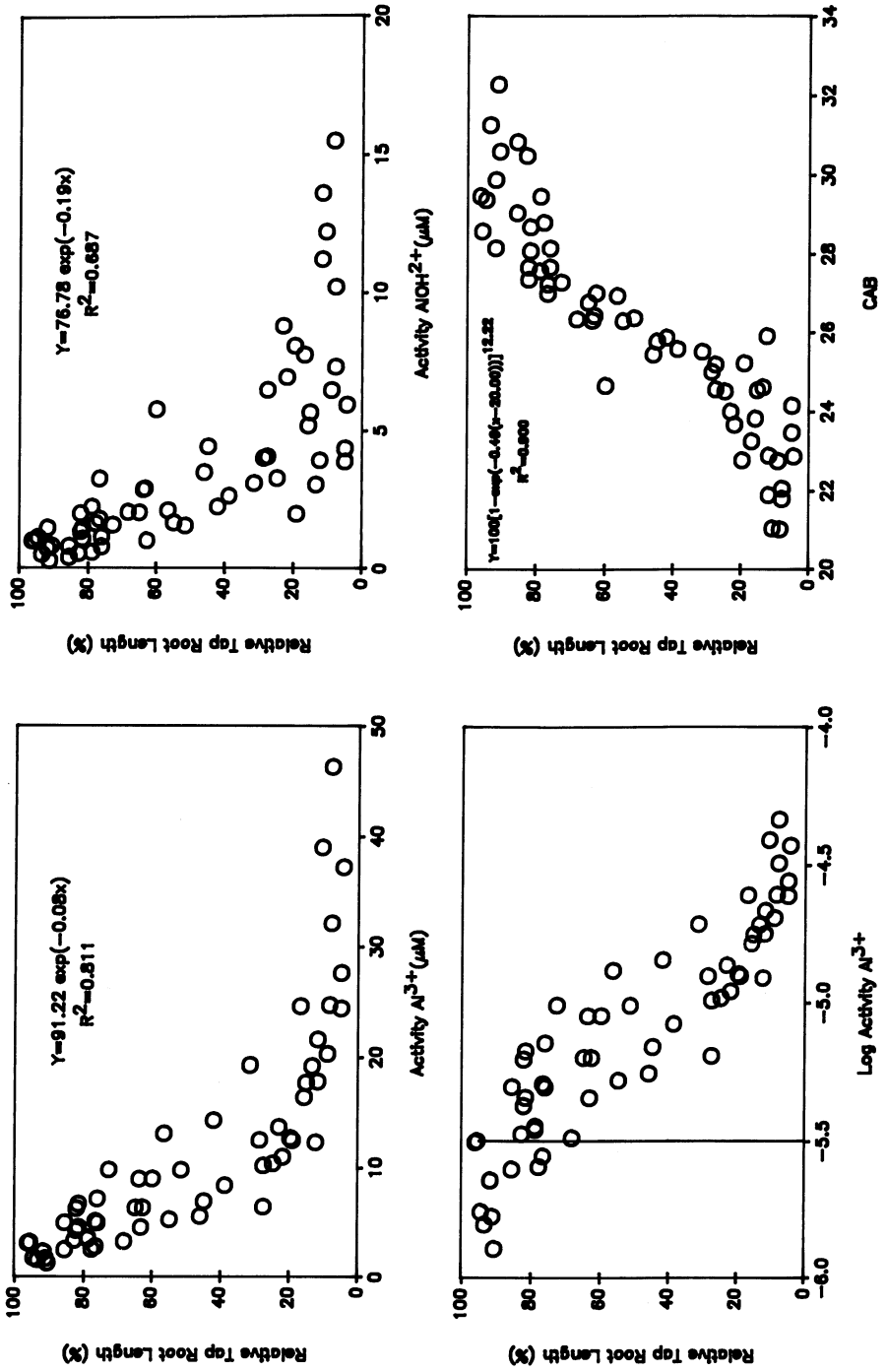

Fig. 19. Effect of Al and Ca activities on soybean root growth in nutrient culture solution (Noble et al. 1988)

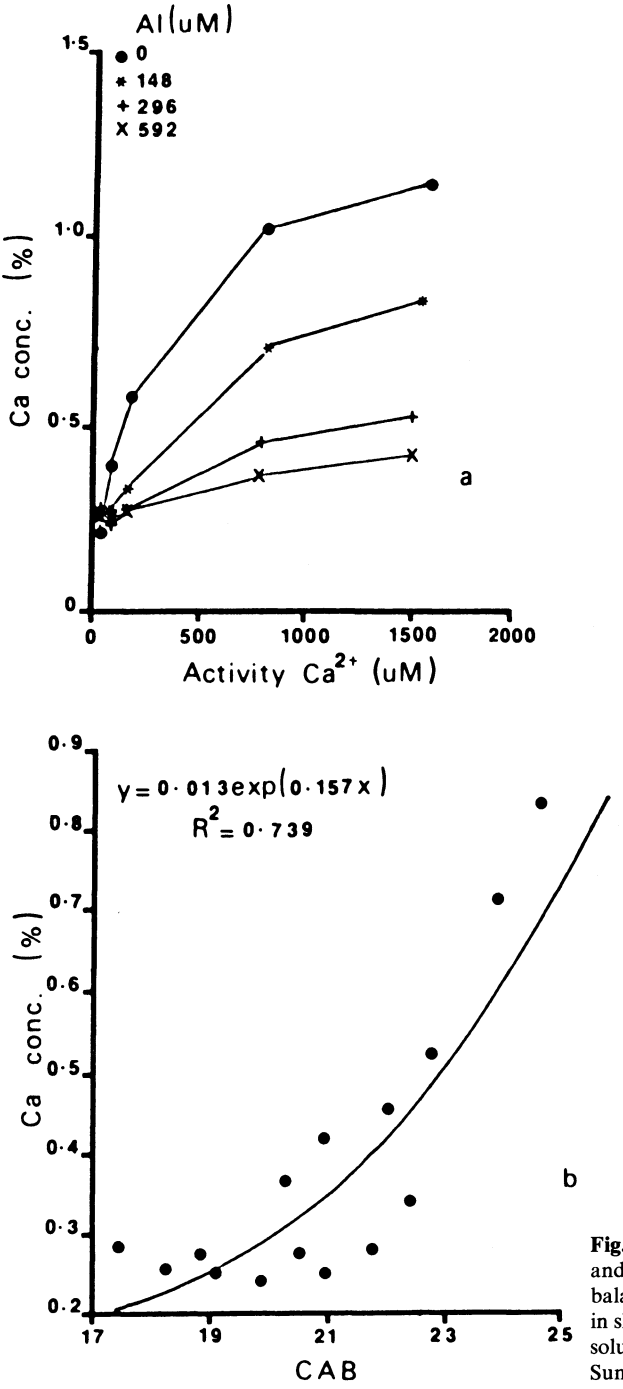

Fig. 20. Effect of **a** Ca^{2+} activity and **b** CAB (calcium-aluminium balance) on the Ca concentration in shoots of soybeans grown in solution culture (Noble and Sumner 1988)

changes in the localized microenvironment such as may occur in the rhizosphere than single-ion activities or concentrations. The extent to which a particular expression for a chemical potential is useful will depend upon the wisdom with which it is constructed from ionic species and stoichiometries (including, possibly, a consideration of ionic potentials and not just valence). Multi-mineral solubility buffering of the soil solution as well as multi-ion competition for uptake sites may demand that such expressions be formulated in a more complex way than has hitherto been the case. There will also have to be more thorough attention paid to comprehensive chemical analysis of soil solutions if single-ion activities are to be reasonably valid (for example our analyses have confirmed that a computation of Al^{3+} activity without taking even a very small amount of soluble fluoride into account may be grossly in error). At the very least, chemical potentials of elements dissolved in soil solutions are a useful basis for comparing the chemical properties of different soils and the way in which plants respond to them. The greatly improved basis for their measurement and computation which is now available should encourage much more widespread and refined use in future soil fertility studies.

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